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THE MAGNITUDE OF THE MAXIMUM CURRENT
ON A ROTATING ELECTRODE

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/Figures are appended./

V. G. Levich [1] recently gave a general quantitative theory of the transfer of a substance in a mixed solution which has great importance in the theory of concentration polarization. In the practical and important case of a rotating disc electrode of sufficient dimension, the theory permits one to find an exact solution of the diffusion equations for the laminar motion of a liquid.

According to Levich's theory, the layer of the solution around the electrode, in which the fundamental variation in concentration occurs (the so-called diffusional layer), is situated within the layer with delayed movement (Prandtl's boundary layer). The concentration of the solution in the diffusion layer varies linearly with increasing distances from the surface in the first approximation. Thus, the exact theory for the magnitude of the maximum current leads to a relation close to that which arises from Nernst's qualitative theory:

$$i_L = n F_c D \frac{1}{\delta},$$

where i_L is the magnitude of the maximum current; δ is the thickness of the diffusion layer; D is the coefficient of diffusion; c is the concentration of the solution; F is Faraday's number; and n is the number of electrons participating in the reaction. But, as opposed to Nernst's theory, Levich's theory permits one to calculate the magnitude of δ theoretically. Furthermore, the latter appears dependent not only on the motion, but also on the coefficient of diffusion. For the electrolyte $A_{z_2} B_{z_1}$ in the case of a disc electrode, the theory gives the following expression for the maximum density of the current:

$$i_L = \frac{(z_1 + z_2) n F D_i c}{z_2 1.62 \left(\frac{D}{\nu}\right)^{1/3}} \left(\frac{\omega}{\nu}\right)^{1/2}, \tag{1}$$

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where z_1 and z_2 are the valences of the cation and anion; ω is the angular velocity of rotation equal to $2\pi m$, where m is the number of revolutions per second; D is the kinematic viscosity of the liquid; the magnitude c is expressed in moles of cation A per cm³: $D = \frac{(z_1 + z_2) D_1 D_2}{z_1 D_1 + z_2 D_2}$ is the effective

coefficient of diffusion of the electrolyte; D_1 is the coefficient of diffusion of the reacting ion; and D_2 is the coefficient of diffusion of the second ion.

An even simpler expression for the magnitude of the maximum current is obtained in the following case: when the ion, whose diffusion determines the magnitude of the maximum current, is in solution with a large surplus of similar ions, sufficient (for the given mobility of ions) enough to disregard the effect of the electrical field on the movement of ions limiting the speed of the process. For this case

$$i_L = 0.617 n F D \, \nu^{-1/2} \omega^{1/2} c.$$

(2)

This same expression, evidently, is also valid for the case of the diffusion of neutral particles.

Thus it follows from Levich's theory that the diffusion layer on a disc electrode has the same thickness over the entire surface

$$\delta = 1.62 \, D^{1/3} \nu^{1/6} \omega^{-1/2}.$$

(3)

As Levich demonstrated, the material in the literature qualitatively confirms this theory well; for quantitative comparison, however, he found no data on experiments carried out under conditions corresponding to those of the theoretical calculation. In later works we also found no corresponding data. In particular, it proved impossible to verify the theory by Van Name's data [3], wherein is measured the speed of dissolution of a cadmium disc in a solution of iodine in KI. The disc in his experiments was fixed on the blade of an agitator, which does not conform to the hydrodynamic conditions of Levich's conclusion.

> NOTE: The conclusion made by Mel'vin - Kh'yuz [2] that the results of these experiments generally contradict the diffusion theory was founded on a misunderstanding: the calculation of the magnitude of δ made by him on the basis of Van Name's data contains a mistake, obtained as the result of the erroneous conversion of the volume expressed in cm into liters. Actually, δ is equal to $2.3 \cdot 10^{-3}$ cm and not 1 cm.)

Therefore it seemed expedient to conduct special experiments for the quantitative verification of the theory. The verification was carried out according to the diffusion of dissolved oxygen toward the electrode, on which the reaction of the cathodic reduction of oxygen was taking place in weak H_2SO_4 solutions. A copper amalgam and a silver electrode were used as cathodes. The copper cathode was in the shape of a cone, whose base (which was the supporting surface) was 4.9 cm² in area and whose height was 1.5 cm. The entire lateral surface of the cone and the shaft to which the cone was fastened were covered by a glass funnel ground down to fit the cone. For sealing the gap, the sleeve was smeared with paraffin for some distance from the edge.

The silver cathode was made in the form of a disc 2.5 cm in diameter, with a steel shaft 0.3 cm in diameter soldered to it. The upper part of the disc and the shaft were insulated with a glyptal lac. After polishing, the magnitude of vibration of the electrode was controlled by an indicator; the amplitude of vibration did not exceed 0.04 mm.

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An anode in the form of a large ring of platinum wire was placed in the horizontal plane passing through the surface of the electrode. The vessel had a volume of 1 liter. The number of revolutions of the electrode could vary from 0.5 to 60 rev/sec.

1. The Amalgamated Electrode

As is known from works on polarography [4], the first stage in the reduction of dissolved oxygen on mercury is the formation of hydrogen peroxide. This reaction was also used by us. The maximum current was determined for each speed of rotation with the aid of a polarization curve. The corresponding curves are reproduced in Figure 1.

The measurements were conducted in 0.05 N sulfuric acid, saturated with atmospheric oxygen. The magnitude of atmospheric pressure was taken into consideration in calculating the solubility of the oxygen. The solubility of oxygen at 76° mm was assumed to equal $2.63 \cdot 10^{-7}$ M/cm^3.

The potential was measured, by the compensation method, against a mercury sulfate electrode.

The measurements were made at room temperature (20±1°C). An exact observation of the constancy of temperature had no importance in our case, because any small fluctuation in temperature and hence corresponding fluctuations in the coefficients of diffusion and viscosity were compensated by corresponding fluctuations in oxygen's solubility.

Oxygen's coefficient of diffusion in a 0.05 N H_2SO_4 solution at 20°C was assumed to equal $1.98 \cdot 10^{-5}$ cm^2/sec. The viscosity of the solution was assumed to equal 10^{-2} cm^2/sec.

The beginning of any new process or behavior at the electrode (for example, the reduction of oxygen to water or the liberation of hydrogen) produced in the region near maximum current a certain deviation in the polarization curve from a strictly vertical rise; in connection with this, the magnitude of the maximum current was assumed by us to equal the current corresponding to the point of discontinuity in the polarization curve. The validity of this situation was verified by the insertion of a correction into the second electrode process, calculated by extrapolating the curve of high voltage values to small current densities.

Figure 2 shows the magnitudes of maximum current, determined by such a method, as a function of the square root of the number of rotations (m), which are compared with the corresponding values calculated with the aid of equation (2) (straight line).

As is evident from the diagram, the values of maximum currents found experimentally differ from the calculated ones by not more than 3%, which does not exceed the total error of the constants used in the calculations. The only exception is the smallest current density (corresponding to the rotation speed of 0.5 rev/sec), which differs from the theoretical value by a somewhat greater magnitude (about 5%). It is evident that the electrode in the given case is already governed by the conditions in which Levich's theory is inapplicable. In the first place, with such small Reynolds' numbers the thickness of Prandtl's boundary layer becomes commensurable with the dimensions of the disc; and in the second place, natural convection may reach a magnitude of the same order as forced convection.

Figure 2 also shows that the experimental data coincide with the theoretical calculated data for rotation speeds of the electrode equal to 40 rev/sec, which corresponds to Reynolds' number Re = 8,000. This is apparently explained by the fact that delay in the beginning of turbulence is characteristic for discs.

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2. The Silver Electrode

The reaction of oxygen reduction at this electrode was affected in 0.01 N H_2SO_4.

Our experiments demonstrated that the magnitude of the maximum current depends on the surface conditons of the silver electrode. If the polarization curve is recorded quickly and is not drawn for large negative potentials or if, before each change, the current is interrupted for the oxidation of silver with oxygen, maximum current values are obtained. These values, correct to 4%, equal those calculated, in the assumption that two electrons participate in the reaction; that is, hydrogen peroxide is formed with the reduction of oxygen (small circles beside the theoretical curve in Figure 3). This assumption was confirmed after electrolysis by the analytical determination of hydrogen peroxide in the solution.

If the electrode is subjected, before the changes to protracted cathodic polarization with high negative potential, then maximum current values are obtained which are one and one-half times as great as the values cited above. These values indicate that on a partially reduced surface of silver approximately one-half of the oxygen is reduced to hydrogen peroxide and one-half to water.

Experiments were also conducted on an oxidized silver electrode with both sides of the disc surface free of the insulating lac film (only the shaft of the disc remained insulated). In this case, a rather significant discrepancy was obtained (about 15%) between the experimental data and the calculated theoretical data, taking into consideration the magnitude of total disc surface (both sides). This discrepancy is related to the presence of the shaft, which changes the hydrodynamics of the upper plane, and also to the presence of the uncovered lateral cylindrical surface of the disc.

Conclusions

1. The maximum current values during the cathodic reduction of dissolved oxygen to hydrogen peroxide were measured, in dependence upon the speed of rotation of a disc electrode in the interval of 0.5 to 47 rev/sec.

The experimental data obtained, within the limits of accuracy of the constants, coincide with the results of the theoretical calculation made on the basis of the theory of diffusion in a mixed liquid, as developed by V. Levich.

2. On an oxidized surface of silver, oxygen is found quantitatively to reduce to hydrogen peroxide; on a partially reduced surface of silver, hydrogen peroxide and water are formed simultaneously.

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/Figures follow/

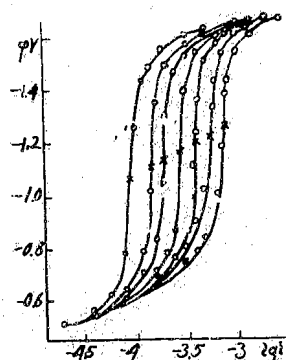CONFIDENTIAL

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Figure 1

Dependence of the electrode potential on the logarithm of current density for various rotation speeds of the electrode. The rotation speeds corresponding to the curves from left to right are as follows: 0.53; 1.5; 2.66; 11.7; 23.4; 40 rev/sec. X are points of discontinuity.

Figure 2

Dependence of the magnitude of the maximum current upon $\sqrt{m}$, where m is the number of revolutions per second of the copper amalgam electrode.
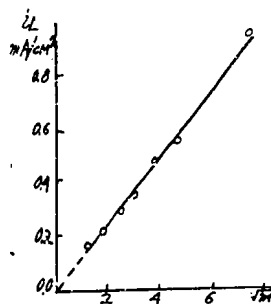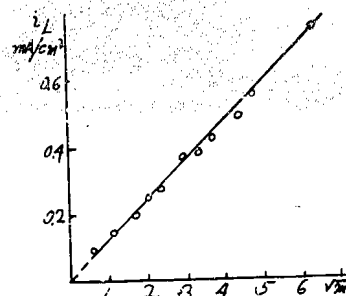

Figure 3

Dependence of the magnitude of the maximum current upon $\sqrt{m}$, where m is the number of revolutions per second of the oxidized silver electrode.

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